

Droplet evaporation and spread on waxy and hairy leaves associated with type and concentration of adjuvants

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Abstract

BACKGROUND: Adjuvants can improve pesticide application efficiency and effectiveness. However, quantifications of the adjuvant-amended pesticide droplet actions on foliage, which could affect application efficiencies, are largely unknown.

RESULTS: Droplet evaporation rates and spread on waxy or hairy leaves varied greatly with the adjuvant types tested. On waxy leaves, the wetted areas of droplets containing crop oil concentrate (COC) were significantly smaller than those containing modified seed oil (MSO), non-ionic surfactant (NIS) or oil surfactant blend (OSB), whereas the evaporation rates of COC-amended droplets were significantly higher. On hairy leaves, COC-amended droplets remained on top of the hairs without wetting the epidermis. When the relative concentration was 1.50, the wetted area of droplets with NIS was 9.2 times lower than that with MSO and 6.1 times lower than that with OSB. The wetted area increased as the adjuvant concentration increased. MSO- or OSB-amended droplets spread extensively on the hairy leaf surface until they were completely dried.

CONCLUSION: These results demonstrated that the proper concentration of MSO, NIS or OSB in spray mixtures improved the homogeneity of spray coverage on both waxy and hairy leaf surfaces and could reduce pesticide use.

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Keywords: deposition; evaporation time; formulation; leaf surface; pesticide; spray coverage; surfactant

1 INTRODUCTION

A thin cuticular membrane (also known as the cuticle) that encloses leaves functions to protect leaves from most environmental hazards.^{1–3} The function also includes the impact of insect pests, pathogens and dust, and the excessive evaporation of water from the plant surfaces.^{1,4–6} The morphological variations that exist among leaf surfaces and structures make it possible to classify them into two categories: leaves that are easy to wet and those that are difficult to wet. The specific characteristics and structures that help to delineate the variations among leaves are the cuticular membrane, waxes, veins, stomata and trichomes. These are all critical to classification of leaves as related to their ability to collect water and other liquids.^{7–9}

For leaves that are difficult to wet, successful application of any pesticides is difficult because of the problem of rebounding droplets that often scatter or roll off the leaves after they come into contact with the surface of the plant. However, some droplets do remain on the surfaces of difficult-to-wet leaves, but they form high contact angles and provide minimal interface between the droplet and the leaf surface. Consequently, application efficiency is decreased and spray usage is increased.^{3,9–11}

Leaves that are difficult to wet often have waxy and hairy surfaces and are highly water repellent.^{1,4,5} Epicuticular waxes occur as crystalline, amorphous and intermediate forms.¹² Leaves that contain crystalline wax are often more hydrophobic and therefore more difficult to wet when sprayed with an aqueous

solution.¹⁰ Leaves with trichomes also are more water repellent than leaves without trichomes, especially when the trichome density is greater than 1 per 25 mm².⁴ The water repellency of trichomes is associated with trichome density and the fact that trichomes prevent water droplets from reaching the epidermis, resulting in relatively low droplet retention on leaves.

Regardless of whether leaves have a waxy or hairy surface, for the foliar application of pesticides to be effective, spray droplets must adhere to the leaf and not bead up and roll off. The applied solution as spray droplets (this includes water) must then first penetrate leaf hairs and waxes on the leaf surface and then into the leaf tissue through cell walls and stomata.^{13,14} Thus, the wettability of a leaf surface is an important factor in the process of deposition, retention and spread of spray droplets on the leaf surface and the penetration of pesticides into the leaf.

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Adjuvants alter spray formulations and enhance the deposition, retention, spread, penetration and uptake of the spray droplets.^{12,15–17} Thus, adjuvants act as humectants and prevent spray droplets from drying too quickly, thereby enhancing the uptake of pesticides in spray droplets through the stomata and cuticular membrane. With the addition of adjuvants, dynamic surface tension rather than equilibrium surface tension has been proposed for the retention of spray droplets. However, adjuvants applied to wettable leaves were reported to have very little effect on spray retention.^{10,18}

Adjuvants have a major effect on the surface tension of spray droplets at the air–liquid interface and on the contact angle at the liquid–plant interface. Oil-based adjuvants (e.g. crop oils, crop oil concentrates and seed oil concentrates) promote the penetration of chemicals through the waxy cuticle. Nitrogen-based fertilizers also have been reported to enhance the uptake of the herbicides.^{2,12,19} Adjuvants function as an activator when: (a) the spread and solubilization of droplets deposited on targets are increased; (b) the epicuticular waxes are dissolved or disrupted; (c) crystal formation in spray deposits is prevented or delayed or an apparent drying out of spray deposits occurs by humectant action; (d) stomatal infiltration is promoted.^{7,12,17,18,20–22}

The concentration of surfactants can influence the efficacy of the spray application. A linear relationship was reported between the retention and the log of surfactant concentration for leaves with crystalline waxes.²³ An increased surfactant concentration from 0.01 to 1% enhanced the overall foliar uptake of pesticides.² However, a high concentration of some surfactants produced a negative effect on pesticide uptake. Different concentrations of the surfactant Mono 0818 produced different uptake threshold peaks for bean and wheat.²² Although adjuvants are usually considered inert, phototoxic effects to some plants were found at surfactant concentrations greater than 0.1%.¹⁴

Understanding how droplets on a leaf surface interact with the leaf surface is important.²⁴ Increased longevity of spray droplets on leaves increases the amount of absorption and uptake of active ingredients of systemic pesticides. Also, greater droplet longevity can prevent crystal formation of the active ingredients. Once droplets are completely evaporated, leaf absorption of chemicals stops, and large crystals form from the chemical residues if the droplets did not evenly spread out on leaves. Crystals may be removed from their impact site by wind, thus further reducing the chemical effectiveness. Therefore, information on pesticide droplet evaporation time and spread on leaf surfaces can assist pesticide formulators to maximize uptake by leaves. Previous investigations on the evaporation and coverage area of pesticide droplets took place in the authors' laboratory with a commonly used surfactant at one concentration on a hydrophobic and hydrophilic glass slide, as well as at different locations on waxy leaves under controlled environmental conditions.^{25–27} This study demonstrated that the dynamics of the evaporation process and the deposition of pesticidal droplets on waxy and hairy leaf surfaces were mainly influenced by three separate components: spray formulation, droplet size and relative humidity. However, the variable conditions in this study only included one surfactant, alkyl polyoxyethylene, in which the droplet diameters ranged from 246 to 886 μm at a relative humidity ranging from 30 to 90%.

The objective of this research was to determine the fate of water droplets amended with different classes of adjuvants at various concentrations on plant leaves. Variables included evaporation times, wetted areas and spread processes of the droplets after their deposition on waxy and hairy leaves of two different

plant varieties using four representative types of adjuvant at five different concentrations.

2 MATERIALS AND METHODS

2.1 Experimental set-up

The experimental system to investigate droplet evaporation and spread on different target surfaces consisted of a droplet generating unit, a target holding chamber, a relative humidity control unit and an image acquisition unit (Fig. 1). A brief description of the system follows, while more details in the description of the unit are presented by Zhu *et al.*²⁸

The droplet generating unit has a capability to produce single droplets of 200–2000 μm diameter. The single droplet was released from a chamfered needle by depressing a trigger pedal. Throughout the tests, adjuvant-amended water droplets of 500 μm diameter were used. The target holding chamber, also known as the environmentally controlled chamber, was insulated from the ambient environmental conditions in the surroundings. The chamber was a rectangular box with an internal volume of 0.56 L. An adjustable target holding platform to position leaf samples on a horizontal x – y axis was placed inside the target holding chamber. Inside the target holding chamber, the conditions were maintained at 25 °C and a relative humidity of 60%. For each test, the abaxial side of a freshly cut leaf sample (2 × 2 cm) was attached to a glass plate with a double-sided adhesive tape, positioned on the adjustable platform, and a single droplet was deposited on the interveinal area of the adaxial surface.

Pictures of the reactions of droplets on leaf surfaces to evaporation and spread were acquired through an image acquisition unit that included a stereoscopic microscope (Model SZX12; Olympus, Japan) with an Insight Firewire[®] attachment to a high-definition digital camera (Model 18.2; Diagnostic Instruments Inc., Sterling Heights, MI). Assessment of these pictures was recorded and saved through the program Image Pro-Plus (v.4.1; Media Cybernetics, Bethesda, MD) at a 4 s interval.

In calculating the spread process of the droplets on waxy and hairy leaves, the time to reach the wetted area (T_{WA}) and the time to remain the aqueous phase of the droplet after deposition (or complete evaporation time, T), were used to characterize the spread process of the droplets. The time (T) for droplet evaporation from a leaf sample was based upon the time required for the acquisition of the total number of sequential images, beginning from droplet disposition to complete droplet evaporation, and the time intervals between each image. For example, the time $t = 0\text{ s}$ indicates the moment when the first photo was taken after the droplet was placed on a leaf surface. In this paper, the wetted area of a droplet is defined by the terminal droplet spread across a leaf surface that produced the maximum contact area between the droplet and the leaf surface. Based on calibrations with a Zeiss 0.01 mm micrometer slide, the wetted area was measured with the ImagePro-Plus Polygonal Hand-trace Feature program (v.4.1; Media Cybernetics, Bethesda, MD). The T_{WA} was defined as the length of time it took from droplet deposition to the moment the wetted area was reached. The T_{WA} was determined by the length of time between the first image of droplet deposition and the first image showing that the wetted area had been reached.

2.2 Plants

Pelargonium stenopetalum Ehrh. (accession number 566), a plant with waxy leaves, and *Pelargonium tomentosum* Jacq. (accession

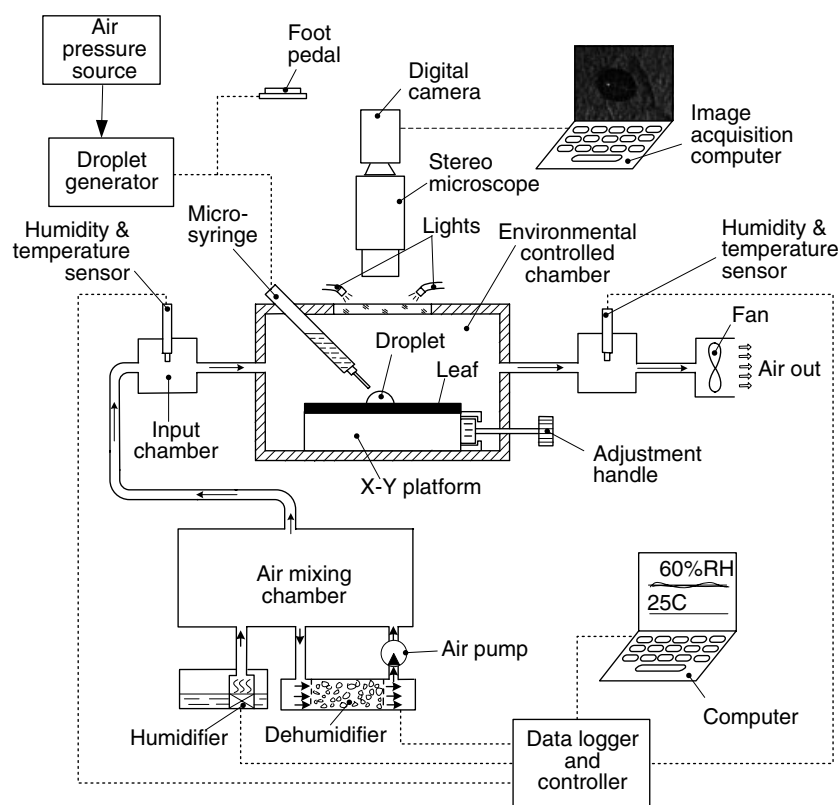


Figure 1. Experimental system to determine the droplet evaporation and spread on a waxy or hairy leaf in an environmentally controlled chamber.

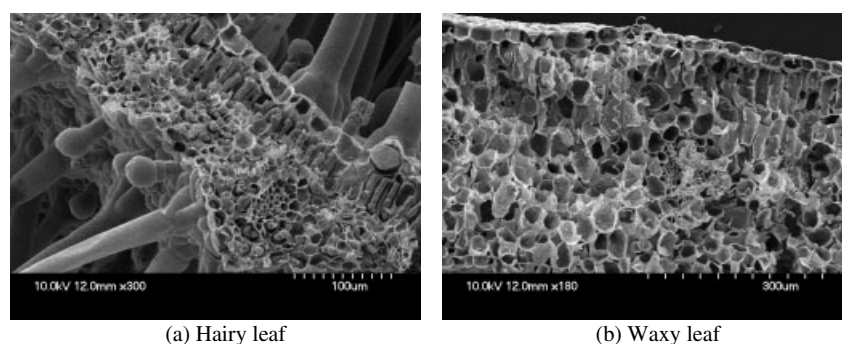


Figure 2. Cross-sections of (a) a hairy leaf (*Pelargonium tomentosum*) and (b) a waxy leaf (*Pelargonium stenopetalum*) observed by scanning electron microscope with 100 \times and 300 \times magnifications respectively.

number 521), a plant with hairy leaves, were obtained from the *Pelargonium* collection of the Ornamental Plant Germplasm Center (OPGC), Columbus, Ohio. Seedlings of both plants were transplanted into two 4 L pots and grown in a greenhouse at a controlled ambient temperature of 25–30 °C. For each experiment, the plants were placed in a growth chamber with a volume of 2.3 m³, and were then exposed to 360 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (14 h duration) light, 18/16 °C (day/night) temperature and 80–85% relative humidity. The plants were automatically watered for 15 min once a day. A representative image of magnified cross-sections of the hairy and waxy leaves is shown in Fig. 2. During the experiment, the contact angle of the water droplet (500 μm diameter) on the adaxial leaf surface in the interveinal area of the leaf was calculated to be 103°. On hairy leaves the mean trichome length was 1.5 mm with a mean density of 10 trichomes mm⁻². There were no contact angle determinations for water droplets on

hairy leaves because the trichomes prevented the droplets from contact with the epidermis.

2.3 Adjuvants

A total of four different types of adjuvant were used (Table 1), including two oil-based adjuvants: crop oil concentrate (COC) and modified seed oil (MSO), a non-ionic surfactant adjuvant (NIS) and a mixture of oil surfactant blend (OSB). The adjuvants were formulated by Wilbur-Ellis Company (San Francisco, CA). Each adjuvant was made into five spray solutions at five different concentrations which were diluted with distilled water (Table 1). The relative concentration (RC) was defined as the ratio between the actual concentration that was applied in order to provide reasonable comparisons among the solutions and the manufacturer-recommended concentration. The RC for the manufacturer-recommended concentration was 1.00. The RCs of

Table 1. Concentration and surface tension of adjuvants at various relative concentrations mixed in distilled water

Adjuvant	Principal chemical composition	Concentration (% v/v)	Relative concentration (RC)	Surface tension (dyne cm ⁻¹)
Crop oil concentrate (COC)	Paraffin-base petroleum oil 83%; surfactant blend 17%	0.26	0.25	38.1
		0.52	0.50	36.5
		1.04	1.00	36.2
		1.56	1.50	35.8
		2.08	2.00	35.8
Modified seed oil (MSO)	Methyl soyate, nonylphenol ethoxylate blend (surfactant content 15%)	0.13	0.25	35.9
		0.26	0.50	35.0
		0.52	1.00	34.8
		0.79	1.50	34.8
		1.04	2.00	34.7
Non-ionic surfactant (NIS)	Alkylphenol ethoxylate, butyl alcohol, dimethylpolysiloxane 90%; ineffective compounds as spray adjuvant 10%	0.06	0.25	30.7
		0.13	0.50	29.6
		0.25	1.00	28.8
		0.38	1.50	29.2
		0.50	2.00	31.2
Oil surfactant blend (OSB)	Ethylated seed oil; 3-(3-hydroxypropyl)-heptamethyltrisiloxane, ethoxylated acetate; polyoxyethylene dioleate; polyol alkyl thoxylate (surfactant content 40%)	0.03	0.25	33.7
		0.06	0.50	32.1
		0.13	1.00	31.4
		0.19	1.50	30.6
		0.26	2.00	30.8
Water only				72.8

the four adjuvants in each of the five amended spray solutions were 0.25, 0.50, 1.00, 1.50 and 2.00 respectively. Surface tensions of different RC solutions for each adjuvant are reported with the RC in Table 1. A semi-automatic Model 21 Tensiomat[®] tensiometer (Fisher Scientific, Pittsburgh, PA) was used to measure the surface tension. To provide a basis for comparison, water-only droplets were also included as a control in the experiments.

With this experimental design, 42 treatments were tested. Although individually described above, they are summarized here. Treatments included water only and solutions containing four different types of adjuvant at five concentrations on two plant species. For each treatment, five leaves representing five replications were used. Only one droplet of 500 µm diameter was discharged on the adaxial leaf surface for each replication. Results were analyzed using Duncan's multiple range test with ProStat v.3.8 (Poly Software International, Inc., Pearl River, NY). The least significant difference among the treatments was determined at the 0.05 level of significance. An integrated index λ was used to evaluate droplet spread and its resistance to drying. The value of λ was determined by the product of total evaporation time and wetted area.

3 RESULTS AND DISCUSSION

3.1 Spread process

The spread of droplets on leaf surfaces after deposition is dependent on the fine structure of the leaf surface and on whether the droplet is amended with or is without adjuvants. A side view

of a 500 µm droplet at the beginning of its contact on a waxy leaf surface with or without an MSO amendment is shown in Fig. 3. With MSO, the spherical droplet on the waxy leaf surface flattened out as a segment of a sphere (Fig. 3a), while the droplet without MSO remained spherical (Fig. 3b). In contrast, a droplet with or without the MSO adjuvant on the hairy leaf is shown in Fig. 4. The 500 µm droplet amended with MSO penetrated and spread among the trichomes (Fig. 4a), while the spherical shape of the non-amended water-only droplet was suspended on trichomes (Fig. 4b). The droplet amended with adjuvant also spread out more extensively on the hairy leaf surface than it did on the waxy leaf surface.

Data in Table 2 show the time to reach the wetted area (T_{WA}) and the complete evaporation time (T) of the 500 µm droplets with and without the adjuvants COC, MSO, NIS and OSB at five RCs on waxy and hairy leaves. There were three possible outcomes for the droplet spread on a leaf surface. One outcome was that the droplets did not spread at all, or that they completely spread out in less than 4 s after deposition (the interval time of sequential images was set at 4 s). In this case, the T_{WA} value was zero. For example, the wetted area of a droplet in an aqueous solution containing COC, set at an RC of 1.00, on a waxy leaf surface did not change from the first to the last picture throughout sequential images (Figs 5a1 to a5). In the second outcome, a droplet, after deposition, reached the wetted area and remained essentially unchanged, or the droplet inside the wetted area slowly receded and completed the evaporation process. This occurred in the droplet spread process with MSO at an RC of 1.50 on the waxy

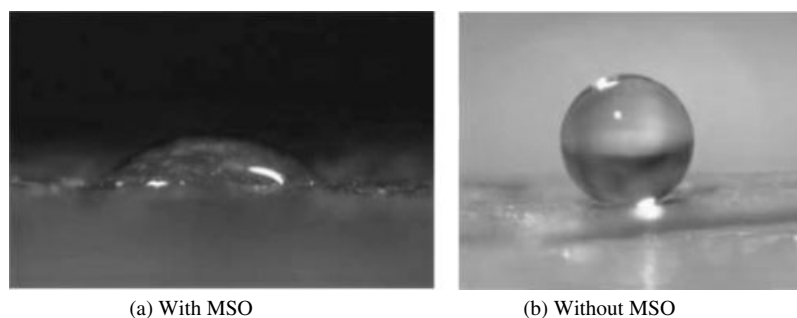


Figure 3. A 500 µm water droplet (a) with and (b) without the adjuvant MSO on the surface of a waxy leaf.

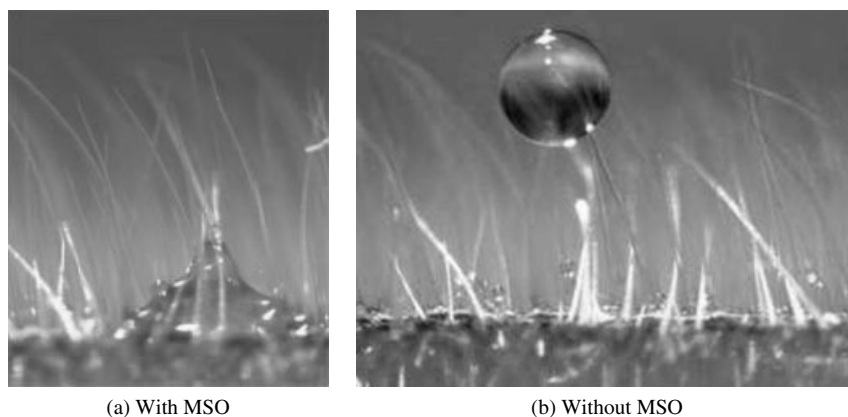


Figure 4. A 500 µm water droplet (a) with and (b) without the adjuvant MSO on the surface of a hairy leaf.

Table 2. The evaporation time (T) and the time to reach the wetted area (T_{WA}) for 500 µm diameter droplets with and without the adjuvants COC, MSO, NIS and OSB at five relative concentrations (RCs) on waxy and hairy leaves^a

Adjuvant	RC	On waxy leaf		On hairy leaf	
		T (\pm SD) (s)	T_{WA}^b (\pm SD) (s)	T^c (\pm SD) (s)	T_{WA}^c (\pm SD) (s)
COC	0.25	223 (\pm 51) abc	0	N/A	N/A
	0.50	218 (\pm 43) abcd	0	N/A	N/A
	1.00	232 (\pm 62) ab	0	N/A	N/A
	1.50	249 (\pm 60) a	10 (\pm 7) d	N/A	N/A
	2.00	259 (\pm 67) a	18 (\pm 16) cd	N/A	N/A
MSO	0.25	189 (\pm 42) bcde	21 (\pm 5) bcd	98 (\pm 25) e	74 (\pm 12) ab
	0.50	200 (\pm 21) bcde	24 (\pm 11) bcd	79 (\pm 13) f	72 (\pm 13) ab
	1.00	190 (\pm 20) bcde	31 (\pm 17) abcd	59 (\pm 9) gh	59 (\pm 9) bc
	1.50	188 (\pm 20) bcde	21 (\pm 16) bcd	50 (\pm 14) h	49 (\pm 14) c
	2.00	181 (\pm 12) cde	42 (\pm 38) ab	54 (\pm 19) gh	54 (\pm 19) bc
NIS	0.25	178 (\pm 12) cde	9 (\pm 4) d	140 (\pm 9) ab	17 (\pm 9) d
	0.50	181 (\pm 12) bde	9 (\pm 3) d	140 (\pm 10) ab	29 (\pm 9) d
	1.00	187 (\pm 17) bcde	13 (\pm 3) d	143 (\pm 7) a	14 (\pm 6) d
	1.50	175 (\pm 33) cde	15 (\pm 9) cd	124 (\pm 5) bc	12 (\pm 15) d
	2.00	181 (\pm 15) bde	9 (\pm 4) d	146 (\pm 15) a	7 (\pm 3) d
OSB	0.25	149 (\pm 22) e	29 (\pm 10) abcd	130 (\pm 11) abc	91 (\pm 35) a
	0.50	160 (\pm 14) e	48 (\pm 33) a	113 (\pm 7) ce	90 (\pm 10) a
	1.00	168 (\pm 25) de	36 (\pm 21) abc	70 (\pm 14) fg	66 (\pm 10) bc
	1.50	181 (\pm 24) bde	21 (\pm 12) cd	58 (\pm 7) gh	58 (\pm 7) bc
	2.00	189 (\pm 18) bcde	18 (\pm 4) cd	58 (\pm 12) gh	58 (\pm 11) bc
Water only		226 (\pm 19)	0	N/A	N/A

^a Means in a column followed by a different letter are significantly different ($P < 0.05$).

^b If T_{WA} is 0 s, then the droplet completed its spread to reach the wetted area before the first picture of a sequential image was taken.

^c N/A: not available because the droplets were suspended on trichomes.

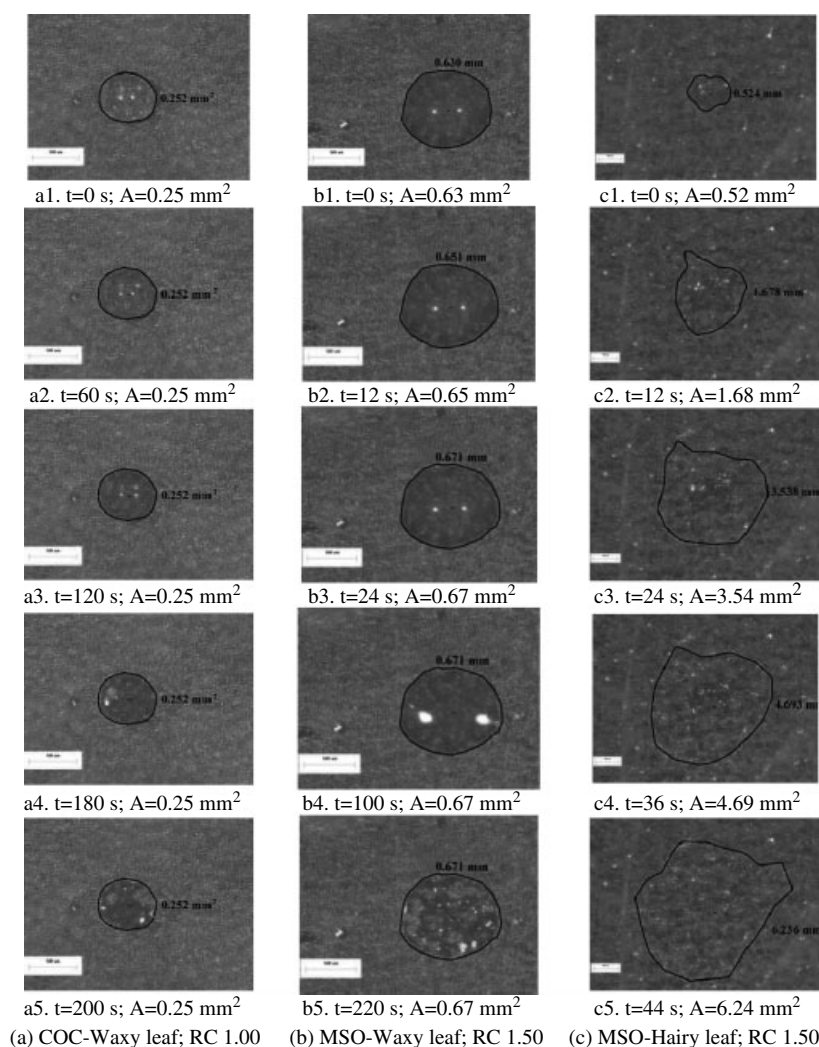


Figure 5. The process of 500 μm droplet spread with (a) COC at a relative concentration (RC) of 1.00 on a waxy leaf (magnification 50 \times), (b) MSO at an RC of 1.50 on a waxy leaf (magnification 50 \times) and (c) MSO at an RC of 1.50 on a hairy leaf (magnification 25 \times).

leaf (Figs 5b1 to b5). The droplet spread reached 0.63 mm^2 after the first image was taken, promptly slowed down its expansion to a maximum wetted area of 0.67 mm^2 at 24 s after deposition and then remained unchanged until 180 s just before the droplet completely evaporated. In this case, the time for the droplet spread process was only a small proportion of the total evaporation time of the droplet. The last outcome was when a droplet, after deposition, spread continuously until near or up to the moment when the droplet completely dried (Figs 5c1 to c5). In this case, the wetted areas of droplets with MSO after deposition on the hairy leaves at an RC of 1.50 were 0.52 mm^2 at 0 s, 1.68 mm^2 at 12 s, 3.54 mm^2 at 24 s, 4.69 mm^2 at 36 s and 6.24 mm^2 at 44 s.

As the data in Table 2 indicate, the T_{WA} of all maximum droplet spread with COC in a RC range of 0.25–1.00 was zero on the waxy leaf, and was as described in the first case. When droplets contained MSO, NIS or OSB (all three for the waxy leaf and only NIS for the hairy leaf) were used, the wetted area was reached in a relatively short time and then remained unchanged or slowly receded from the wetted area until evaporation was completed (see the second case described above). The droplets with MSO or OSB continuously spread after deposition, even up to the moment of complete evaporation (the third case described above). For

example, the ratio between the T_{WA} of a droplet with NIS and its total evaporation time at an RC of 1.50 on the waxy and hairy leaves was 0.09 and 0.10 respectively. However, an even higher ratio of 0.98 and 1.00 for MSO and OSB at the same RC of 1.50 for the hairy leaf was obtained.

3.2 Evaporation time

Evaporation times of the droplets with COC and water only on the waxy leaves were nearly the same, but at RCs of 1.50 and 2.00 they were significantly longer than those evaporation times of the other adjuvants (MSO, NIS and OSB) at any concentration (Table 2). The longest evaporation times among the five different RC rates were 259, 200, 187 and 189 s for COC, MSO, NIS and OSB respectively. The effect of the concentration on evaporation time was noticeable, but not significant. The largest differences in evaporation time among the five RCs for the adjuvants COC, MSO, NIS and OSB were 16, 10, 6 and 21% respectively. For droplets of similar sizes and on similar surfaces, the expectation is that, the greater the wetted area, the shorter will be the evaporation time. The evaporation time tended to increase along with an increase in RC for the adjuvants COC and OSB, or droplets with COC and OSB at a higher RC were more likely to resist drying, but not significantly.

Table 3. The wetted area of 500 μm diameter droplets with and without adjuvants COC, MSO, NIS and OSB at five relative concentrations (RCs) on waxy and hairy leaves^a

Adjuvant	RC	Wetted area (\pm SD) (mm^2)	
		On waxy leaf	On hairy leaf ^b
COC	0.25	0.19 (\pm 0.05) f	N/A
	0.50	0.18 (\pm 0.07) f	N/A
	1.00	0.22 (\pm 0.05) f	N/A
	1.50	0.30 (\pm 0.12) ef	N/A
	2.00	0.25 (\pm 0.10) ef	N/A
MSO	0.25	0.46 (\pm 0.11) cd	1.65 (\pm 0.08) d
	0.50	0.56 (\pm 0.12) abcd	3.37 (\pm 1.81) c
	1.00	0.56 (\pm 0.14) abcd	5.16 (\pm 0.72) ab
	1.50	0.60 (\pm 0.11) ab	6.52 (\pm 2.13) a
	2.00	0.58 (\pm 0.11) abc	6.51 (\pm 2.20) a
NIS	0.25	0.45 (\pm 0.04) d	0.55 (\pm 0.06) d
	0.50	0.47 (\pm 0.054) cd	0.61 (\pm 0.05) d
	1.00	0.57 (\pm 0.09) abcd	0.64 (\pm 0.09) d
	1.50	0.49 (\pm 0.10) bcd	0.71 (\pm 0.06) d
	2.00	0.49 (\pm 0.04) bcd	0.62 (\pm 0.08) d
OSB	0.25	0.34 (\pm 0.08) e	0.64 (\pm 0.11) d
	0.50	0.51 (\pm 0.06) bcd	1.32 (\pm 0.34) d
	1.00	0.57 (\pm 0.08) abcd	3.23 (\pm 1.01) c
	1.50	0.68 (\pm 0.04) a	4.35 (\pm 0.94) bc
	2.00	0.56 (\pm 0.06) abcd	5.36 (\pm 0.72) ab
Water only		0.14 (\pm 0.01)	N/A

^a Means in a column followed by a different letter are significantly different ($P < 0.05$).

^b N/A: not available. Droplets were suspended on trichomes.

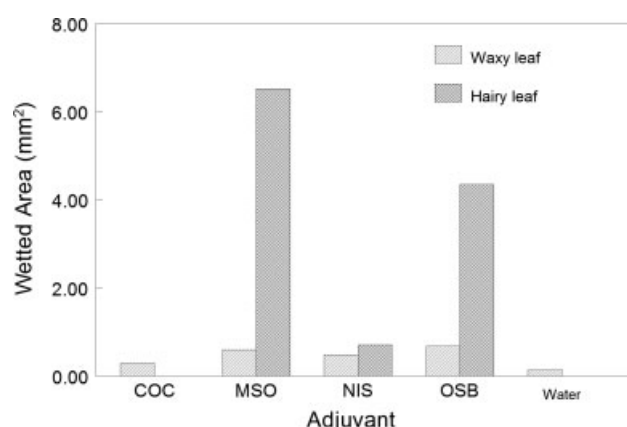


Figure 6. Wetted area of 500 μm droplets with COC, MSO, NIS and OSB at an RC of 1.50 on waxy and hairy leaves (□ waxy leaf; ■ hairy leaf).

For the hairy leaf, the longest evaporation times among the five RCs for adjuvants MSO, NIS and OSB were 98, 146 and 130 s respectively. The differences in the evaporation time among the five RCs were 49, 15 and 55%. The evaporation time with NIS was generally higher than that with MSO or OSB, because the droplets with NIS had a significantly lower wetted area.

3.3 Wetted area

The wetted areas of 500 μm diameter droplets without and with the adjuvants at different relative concentrations (RCs) on waxy and hairy leaves are presented in Table 3. On a waxy leaf, the wetted areas of the droplets with the adjuvants significantly improved over those of the water-only droplets. The wetted area of the droplets with COC was obviously smaller than that with any other adjuvant. There was no significant difference in the wetted area among the three adjuvants MOS, NIS and OSB. Compared with the mean wetted area of water-only droplets, there was an increase of 36 and 386% for COC at an RC of 0.25 and for OSB at an RC of 1.50 respectively. Also, water-only droplets did not spread on the waxy leaf surfaces, with the wetted area measuring only 0.14 mm^2 . When an adjuvant was added to the water droplets, the droplet spread significantly improved. At an RC of 0.25, the wetted area of adjuvant-amended droplets increased by 36, 229, 221 and 143% for COC, MSO, NIS and OSB respectively. The largest wetted area was 0.30, 0.60, 0.57 and 0.68 mm^2 for COC, MSO, NIS and OSB adjuvants with the corresponding RC of 1.50, 1.50, 1.00 and 1.50 respectively. The effect of adjuvant concentration increased the wetted areas of droplets, but the increase was not significantly great (Fig. 6). The differences between the smallest and largest maximum wetted areas among the five different RCs were 40% (with COC), 23% (MSO), 21% (NIS) and 50% (OSB), even though there was a sevenfold increase from 0.25 to 2.00 RC of the adjuvants.

On hairy leaves, water-only droplets or those amended with COC at 0.25–2.00 RC were unable to breach the hairy surface and reach the epidermis. However, MSO- or OSB-amended droplets were able to reach and adhere to the leaf surface. Also, there were significant differences in droplet spread from different adjuvants. The droplet with COC remained spherical, even at 2.00 RC, and was trapped by the trichomes (Fig. 7a). Furthermore, even as droplet size decreased via evaporation, the droplets were still trapped by the trichomes (Fig. 7b). When compared with MSO- and OSB-amended droplet spread, the droplet spread with NIS adjuvant was significantly smaller (9.2- and 6.2-fold respectively) at an RC of 1.50, which further confirmed that the effect of adjuvant concentration on droplet spread on hairy leaves varied with the type of adjuvant.

Also, on hairy leaves a larger wetted area correlated with a higher RC. However, the wetted area of droplets with MSO or NIS did not increase with increased RC once it peaked (Fig. 8). For example, the largest wetted area of a NIS-amended droplet was 0.71 mm^2 at an RC of 1.50 but not 2.00 (Table 3). The wetted area with the adjuvant MSO continuously increased from 1.65 mm^2 to the peak value of 6.52 mm^2 , along with the RC, which increased from a rate of 0.25 up to 1.50. However, when the RC was raised to 2.00, MSO failed to increase in value. When OSB was added to the water droplets, the wetted area increased consistently and proportionately to the increase in RC: the wetted area increased by 738% when the RC increased from 0.25 to 2.00 (Table 3). The wetted area significantly increased with rising RC for the hairy leaf: 295% at 1.50 RC, 29% at 1.50 RC and 737% at 2.00 RC with MSO, NIS and OSB respectively.

Data in Table 3 also show comparison between wetted areas of droplets on a set of waxy and hairy leaves exposed to the same adjuvant concentration (excluding COC). Generally, the wetted areas on hairy leaves were greater than those on waxy leaves. For example, with MSO the wetted areas on the hairy leaves were 3.6, 6.0, 9.2, 10.9 and 11.2 times greater for RC at 0.25, 0.50, 1.00 and 1.50, respectively, than those on the waxy leaves. However, the wetted areas with NIS on the hairy leaf were only 1.2, 1.3, 1.1,

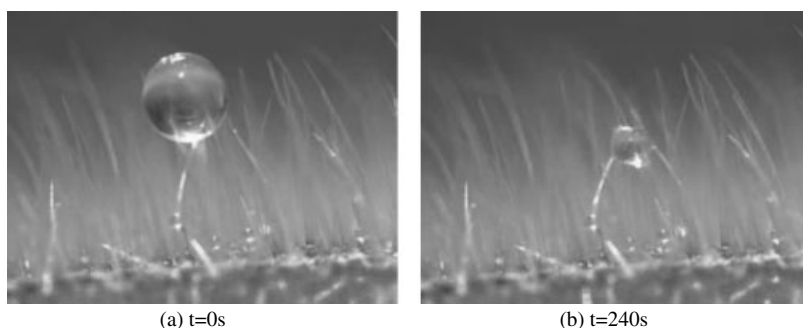


Figure 7. A 500 μm droplet with COC at an RC of 2.00, suspended on the trichomes of a hairy leaf at 0 s (a) and 240 s (b) after deposition.

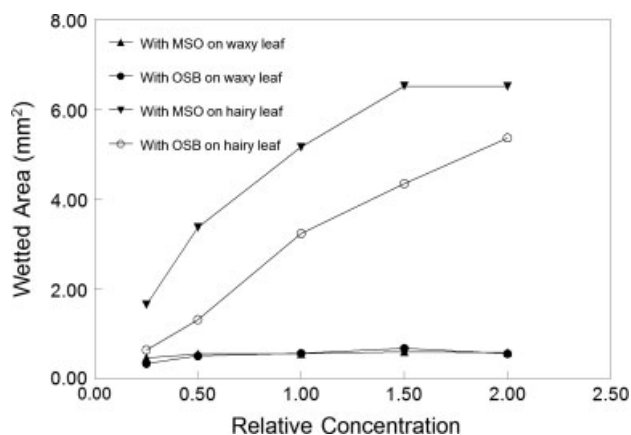


Figure 8. Wetted area of 500 μm droplets at relative concentration (RC) rates ranging from 0.25 to 2.00, with MSO or OSB on waxy and hairy leaves (▲ with MSO on a waxy leaf; ● with OSB on a waxy leaf; ▼ with MSO on a hairy leaf; ○ with OSB on a hairy leaf).

1.4 and 1.3 times greater than those on waxy leaves at the same five RCs. Figure 6 shows the wetted areas on both waxy and hairy leaves with the other adjuvants (COC, MSO, NIS and OSB) at an RC of 1.50. On hairy leaves, the wetted areas with the adjuvants MSO and OSB were 6.52 and 4.35 mm^2 and far greater than with the other adjuvants. In comparison with waxy leaves, the wetted areas with the adjuvants MSO and OSB on the hairy leaves were 987 and 540% greater, respectively, than those on the waxy leaves. However, the adjuvant NIS showed an increase in wetted area on hairy leaf of only 45% compared with waxy leaf.

Owing to the fact that the wetted area increased by using adjuvants, the spray coverage area per volume of spray applied on leaf surfaces can be increased by using the adjuvants, offering a possible reduction in the amount of spray mixtures applied. For example, the mean wetted area of a 500 μm diameter water-only droplet on the waxy leaf surface was 0.14 mm^2 , and it was 0.56 mm^2 when 1.00 RC MSO was added. A 4000 mm^2 leaf surface would require 28 571 water-only droplets of 500 μm diameter (equivalent to 1.87 mL) to cover the leaf surface completely. However, for the same leaf surface, it would require only 7143 droplets of 500 μm diameter (equivalent to 0.47 mL) when MSO was used, a 4.0-fold reduction in spray volume. Therefore, the use of adjuvants increased the ratio between the coverage area and the amount of spray required, offering increased application efficiency and reduced pesticide use. Consequently, less pesticide usage would be economically beneficial to growers and ecologically beneficial to people and the environment.

The droplets that contained MSO or OSB had a great ability to spread quickly on the hairy leaf, starting from the deposition of a droplet and continuously spreading up to the moment of complete evaporation. These two adjuvants may be able to disrupt or dissolve the waxes on the surface of the trichomes and leaf epidermis. Consequently, this would help to enhance the spread and penetration of spray droplets.

Surface tensions of droplets containing COC, MSO, NIS and OSB at 0.25, 0.50, 1.00, 1.50 and 2.00 RC are reported in Table 1. Surface tension was a factor that affected droplet spread. When the surface tension was low, the wetted area was high. However, equilibrium surface tension is not the only index that determines droplet spread. Spread performance is also affected by other factors that are independent of surface tension. As reported here, they included species of plant, leaf surface structure, type of adjuvant and its concentration. For example, the surface tension of the water-only droplets was calculated to be 72.8 dyne cm^{-1} . However, when the adjuvant COC was added at an RC of 2.00, the surface tension dropped by 37 dyne cm^{-1} to 35.8 dyne cm^{-1} , but the wetted area did not increase as much as the reduction rate in surface tension.

In general, a larger droplet spread area increases uptake of pesticides in the target plants. Also, extending the liquid state of droplets aids the penetration of active ingredients into leaf tissues. However, these two desirable conditions are at odds with each other (i.e. a larger wetted area occurred with less evaporation time). For easy comparison of the effectiveness of different adjuvants based on these two criteria, the integrated index, λ , which is the product of wetted area and evaporation time, was summarized for each treatment (Table 4). The λ values (42–79 s mm^{-2}) of COC on the waxy leaf were clearly lower than those of any other adjuvant on the waxy or hairy leaves. For NIS, the λ values were 79–106 s mm^{-2} on the waxy leaf, but were closer to 77–90 s mm^{-2} on the hairy leaf. For the MSO or OSB adjuvant, the λ value was slightly higher than the NIS on the waxy leaf. However, when it came to the hairy leaf, the value was much higher than that with NIS. The highest λ value was 324 s mm^{-2} with MSO at an RC of 2.00, with OSB following at 303 s mm^{-2} in the RC range of 2.00. The λ for the droplet on the hairy leaf was 7.7 times larger when MSO was used at an RC of 2.00 than with COC at an RC of 0.50 on the waxy leaf.

4 SUMMARY AND CONCLUSIONS

The evaporation and wetted area of 500 μm droplets on the waxy and hairy leaves along with four classes of adjuvant (COC, MSO, NIS and OSB) at five concentrations were investigated in this study. Specific conclusions are as follows.

Table 4. The integrated index λ (the product of total evaporation time and wetted area) of 500 μm droplets with and without the adjuvants COC, MSO, NIS and OSB at five different relative concentration (RC) levels on waxy and hairy leaves

Adjuvant	RC	Integrated index λ (\pm SD) (s mm^{-2})	
		On waxy leaf	On hairy leaf ^a
COC	0.25	44 (\pm 22)	N/A ⁽¹⁾
	0.50	42 (\pm 27)	N/A
	1.00	52 (\pm 25)	N/A
	1.50	79 (\pm 51)	N/A
	2.00	70 (\pm 45)	N/A
MSO	0.25	91 (\pm 40)	152 (\pm 64)
	0.50	112 (\pm 31)	251 (\pm 89)
	1.00	107 (\pm 35)	304 (\pm 46)
	1.50	113 (\pm 25)	302 (\pm 55)
	2.00	106 (\pm 25)	324(59)
NIS	0.25	79 (\pm 3)	77 (\pm 6)
	0.50	84 (\pm 8)	86 (\pm 12)
	1.00	106 (\pm 15)	90 (\pm 10)
	1.50	84 (\pm 12)	87 (\pm 7)
	2.00	88 (\pm 9)	90 (\pm 12)
OSB	0.25	51 (\pm 19)	83 (\pm 12)
	0.50	81 (\pm 10)	147 (\pm 35)
	1.00	95 (\pm 20)	214 (\pm 30)
	1.50	123 (\pm 24)	251 (\pm 44)
Water only	2.00	105 (\pm 18)	303 (\pm 37)
		31 (\pm 1)	N/A

^a N/A: not available because the droplets were suspended on trichomes.

The wetted area, along with the evaporation time, of the droplets varied with the leaf surface and the type and concentration of adjuvants used. In general, the wetted area increased with adjuvant concentration, but it peaked at a specific concentration for each adjuvant on either the waxy or the hairy leaf (excluding OSB on the hairy leaf). The differences in the wetted area and the evaporation time were not significantly different among all five RCs for any adjuvant on the waxy leaf. The greatest difference was only about 50% in the wetted area with OSB, and only 21% in the droplet evaporation time. However, on the hairy leaf there were significant differences in the wetted area (88%) and the evaporation time (55%) that followed for OSB, while these differences were 23% and 15%, respectively, for NIS.

The differences in the wetted area and evaporation time among MSO-, NIS- and OSB-amended droplets on waxy and hairy leaves were not significant.

On the waxy leaf, the wetted area of the droplet with COC was significantly lower than that with MSO, NIS or OSB. The evaporation time with COC at 1.50 and 2.00 RC was significantly higher than that of any other adjuvant. The integrated index for the droplets with COC was lower than with any other adjuvant at any RC, excluding OSB at an RC of 0.25.

On the hairy leaf, the 500 μm diameter droplets with COC were often held by the trichomes, consequently not reaching the epidermal surface of the leaf. The wetted areas with MSO or OSB were 9.2 and 6.1 times greater when compared with that with NIS at the same RC of 1.50. The greatest integrated indices among

the five RCs were 324 and 303 s mm^2 for MSO and OSB, but the integrated index was only 90 s mm^2 for NIS.

This study clearly demonstrates the fact that the use of adjuvants could greatly improve the homogeneity of sprayed pesticides to increase the coverage area on target surface, thereby offering possibilities of reduced pesticide usage, and leading to economic benefit to the farmer and reduced risk of contamination of the environment by pesticides. Because droplet behaviors vary with the fine structures of leaf surfaces and spray mixture properties, recommendations for optimum biological effects and reduced pesticide use would be different for different leaf surfaces and spray formulations.

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